Simulation of X-ray Diffraction Patterns

John L. Barber, T-1

For more than a century the experimental technique of X-ray diffraction has been an invaluable tool for both diagnostics and imaging of diverse types of samples. However, there is often a need to generate an X-ray diffraction pattern corresponding to a given hypothetical experimental setup without directly performing the actual experiment. Such a need arises, for example, in the design of experiments or experimental facilities, or in the analysis or validation of large-scale molecular dynamics (MD) simulations. In this highlight, I give a brief overview of some recent efforts in the computer simulation of X-ray diffraction patterns produced from arbitrary samples and with a wide range of sources and detectors.

Suppose we have a collection of N atoms, with coordinates $\{\vec{x}_j\}$ (in practice this set of atomic coordinates is most often obtained from an MD simulation), as well as the schematic experimental setup shown in Fig. 1. If we assume for the moment that the light source is a monochromatic, unpolarized, coherent beam, it is straightforward to show that the net scattered intensity at a position $\vec{y}$ on the detector is given by

$$I(\vec{y}) = I_o \left(\frac{r_e}{|\vec{y}|}\right)^2 \left(1 - (\hat{\varepsilon}\cdot\vec{y})/|\vec{y}|\right) \cos(2\theta) \left|\sum_{j=1}^{N} Z_j e^{-i\vec{q}\cdot\vec{x}_j}\right|^2 \quad (1)$$

where I_o is the intensity of the source, r_e is the classical radius of the electron, $\hat{\varepsilon}$ is the polarization vector of the source, 2θ is the deflection angle of the beam, Z_j is the atomic number of the j^{th} atom, and the scattering vector $\vec{q} = \vec{k}_j - \vec{k}_i$ is the difference between the final and initial wave vectors of the scattered light.

The various terms in Eq. (1) are straightforward to evaluate, except for the sum over particles, which can only be evaluated by direct "brute-force" means for systems consisting of less than 10,000 particles. For each point $\vec{y}$ on the detector, there corresponds a distinct scattering vector $\vec{q}$. Assuming a 300 x 300 desired resolution in the diffraction pattern, and 10^9 atoms in the sample (a common number in modern MD simulations), this sum amounts to a prohibitive 10^{14} separate terms. Note that although it has the appearance of a Fourier transform, this sum cannot be directly evaluated via fast Fourier transform techniques, since the atomic positions are in general arbitrarily spaced, and thus do not fall precisely on a grid. This problem can be sidestepped, however, via the observation that the sum

$$S(\vec{q}) \equiv \sum_{j=1}^{N} Z_j e^{-i\vec{q}\cdot\vec{x}_j} \quad (2)$$

may be rewritten as

$$S(\vec{q}) = \int d\vec{x}\, e^{-i\vec{q}\cdot\vec{x}}\, \rho(\vec{x})$$

where

$$\rho(\vec{x}) = \sum_{j=1}^{N} Z_j\, \delta(\vec{x} - \vec{x}_j) \quad (3)$$

is the number density of electrons in the sample. Equation (3) may be cast onto a regular grid by approximating each δ function via a suitable "quasi-δ" envelope function. In [1], for example, a Gaussian envelope is recommended, which has the advantage of speed and ease of implementation, but also has the drawbacks that it entails high memory usage (a concern in situations with larger data sets) as well as unavoidable approximations. In this work, a periodic sinc function envelope is used instead, which can be shown to both minimize memory usage, and allow an *exact* evaluation of the sum in Equation (2), at the cost of moderately higher computational time. Some example diffraction patterns generated by these methods from a 5.2-million atom MD simulation of a shock passing through copper and illuminated by a coherent 100 KeV beam are shown in

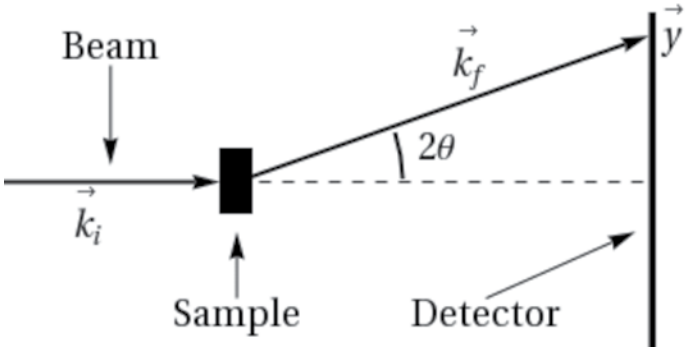

Fig. 1. A schematic diagram of the experimental setup simulated in this work.

Fig. 2. Each diffraction pattern took approximately 10 minutes to generate on a single-processor 3 GHz workstation. Data sets from MD simulations containing up to 40 million particles have been handled without difficulty.

There are a large number of variations of this problem (not described here due to limitations on length) that allow the consideration of, for example, arbitrary polarization spectra (the beam in Fig. 2 is assumed to be unpolarized), arbitrary broadband source spectra (i.e., Laue diffraction), virtual powderization of the sample, and point light source. See the "MPDH CXDI Analysis" page on the MaRIE wiki (http://marie-sp.lanl.gov/wikimarie) for more details.

For more information contact John L. Barber at jlbarber@lanl.gov.

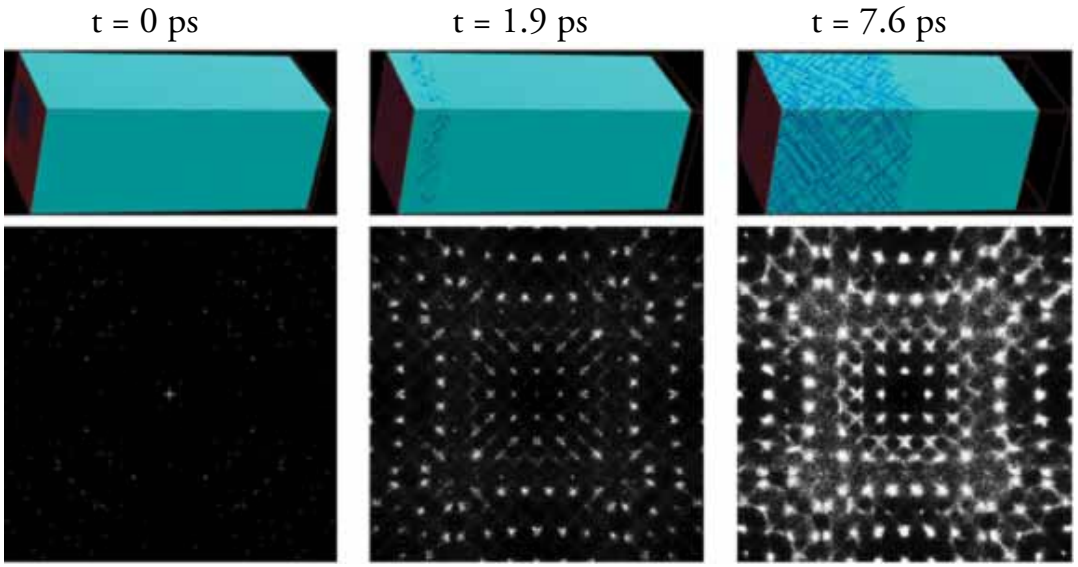

Fig. 2. Three snapshots from a 30 nm x 30 nm x 70 nm, 5.2-million atom MD simulation of a shock passing through FCC copper, along with the simulated X-ray diffraction patterns from each.

[1] G. Kimminau et al., *J. Phys. Condens. Matter* **20,** 505203 (2008).

Funding Acknowledgments
LANL MaRIE Capability Development